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FINAL REPORT
EFFECT OF PLASTICIZERS
ON THE STRENGTH OF A PLASTIC MOTOR CASE

by
Donald A. Morgan

October 1971

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U.S. ARMY MISSILE COMMAND

Redstone Arsenal, Alabama

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This report summarizes the effect of plasticizers on the strength of a glass-fiber-reinforced plastic motor case and, specifically, the effect on the burst strength of the motor case.

Maximum average loss in burst strength occurred with dipropyl adipate and amounted to 79 psi out of an average burst of the blank of 2842 psi. Deterioration did not increase with longer intervals of storage.

A direct correlation could be established between burst pressure and extension at break of a ring cut from an identical (same lot) motor case and treated with plasticizer. In addition, a direct correlation could be established between burst pressure and the reciprocal of the amount of sag of a coupon cut from an identical motor case.

The effect on a motor case after two years storage in contact with a plasticizer is considered negligible.

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SYMBOLS AND ABBREVIATIONS

\bar{M}	Molecular weight
ρ	Density, gm/cc
η	Viscosity, gm/cm ³ -sec
σ	Surface tension, dyne/cm
ν	Kinematic viscosity cm ² /sec
δ	Solubility factor, cal ^{$\frac{1}{2}$} /cm ^{$\frac{3}{2}$}
DMP	Dimethyl phthalate
DEP	Diethyl Phthalate
DBP	Dibutyl phthalate
TEP	Triethyl phosphate
TBP	Tributyl phosphate
TA	Triacetin
TBC	Tributyl citrate
DBT	Dibutyl d-tartrate
EN	Ethyl nonanoate
DBS	Dibutyl sebacate
DBA	Di-isobutyl azelate
DBM	Dibutyl maleate
DPA	Dipropyl adipate
CO	Castor oil
TMETN	Trimethylolethane trinitrate
TEGDN	Trimethylene glycol dinitrate
NG	Nitroglycerine

1. Introduction

Many rocket motor cases have already been made of plastic materials reinforced by wound glass fibers. Wider use of these cases awaits more certain knowledge of the degree of their deterioration during long storage under a variety of conditions.

Work is in progress by many investigators on the deterioration of glass-reinforced plastics by weather during extended exposure. Results are now being published [1, 2, 3, 4, 5].

Weather is not the only environment to which a motor case is subjected. The interior is subjected to a chemical environment consisting of various vapors, liquids, and gases derived from the propellant and from the adhesives, insulation, and other materials used in assembly of a rocket motor. The liner normally used between the propellant and the case gives a high degree of protection, but even this can be slowly penetrated by diffusive processes during long storage.

The storage life of a plastic motor case of a loaded rocket should be at least as long as the propellant it contains. The objective of the research is to determine if the chemical environment on the inside of a loaded rocket motor could contribute to the deterioration of a plastic case, and if so, to what degree, and to provide a method of rapid screening to determine if a given chemical could cause deterioration in the concentration present.

Plasticizers found in a propellant could cause deterioration of the case. These plasticizers are generally organic esters which range from nitroglycerine (NG) to castor oil (CO). Nitrous fumes or other gases may also have an effect.

Any definite conclusions as to the absolute degree of deterioration must await actual long-time storage tests under normal environment.

2. Research Plan and Materials

The experiment is divided into three phases. In Phase I, 17 plasticizers used in the formulation of propellants were tested to determine those most likely to degrade a motor case. In Phase II, those plasticizers found especially active were absorbed on Fuller's Earth and packed into rings cut from a motor case. In Phase III, discussed in this report, plasticizers selected from Phase II were mixed with builder's sand and loaded into the motor case.

At the outset it was postulated that an attack by these plasticizers would be either on the resin or on the glass-resin interface. For this reason the tests in Phases I and II were designed so that little if any

of the tensile strength of the glass fibers was reflected in the results. In Phase III, a burst test was used and the tensile strength of the glass fibers was, of necessity, important.

The test material used in all phases was derived from a single lot of plastic motor cases reinforced by wound fibers of S-glass. Details of raw materials, manufacture, and testing are found in the manufacturer's report [6] and in the previous reports on the subject [7, 8].

The plasticizers used in these experiments were from one lot of practical grade. Values of the physical properties of these plasticizers are found in Table I. Certain physical properties were determined in the laboratory and so may differ from those reported for pure compounds. Values of viscosity used in a subsequent correlation are those found in literature for pure compounds, because these values were found to give a better correlation than actual determined value. Kinematic viscosity was likewise found to give a better fit in the correlation than viscosity alone.

3. Test Equipment and Methods

Test equipment and methods used in Phase I [7], shear-creep of motor case segments immersed in plasticizers, and in Phase II [8], elongation and tensile strength of rings treated with selected plasticizers, have already been reported.

Tests in Phase III consisted of burst tests on plastic motor cases stored in contact with plasticizers selected from Phase II. Plasticizers selected were one of high activity, dipropyl adipate (DPA) of low activity, triethylene glycol dinitrate (TEGDN), and of intermediate activity, dibutyl phthalate (DBP).

These plastic motor cases were of the same lot [6] from which the coupons and rings were derived and had been stored at 76°F and 50 percent relative humidity. The cases were filled with a saturated mixture of builder's sand and plasticizer and stored in an igloo. Samples in triplicate were removed at 6-month intervals for burst. Blanks were stored concurrently and also burst in triplicate.

The plasticizers used easily permeated the cases. Consequently, the cases had to be placed in sealed polyethylene bags during storage. The porosity of the cases is notable. A boot proved necessary in all burst tests. The increases in diameter of the cases during burst were unusual. Increases of 12.5 percent on the circumference at pressures of 2000 psi were not uncommon. All cases burst along a longitudinal axis, as did the original qualification test bottles [6]. Pressurization rates of 1000 psi per minute were used as had been specified for the original tests.

The original scheme called for a statistical analysis to be made on the burst pressures of the three plasticizer series and the blank. A change in organization caused the first series of bursts, and part of the second, to be made by one team on one set of equipment and the remainder of the second series, plus the third and fourth, to be run by a second team on a second set of equipment. This introduced personal errors into the tests. Consequently, analyses were made first on differences between burst pressures of the bottles and the burst pressures of the blanks and secondly over the last three time periods.

a. Results

Results from Phase I are summarized in Table I which presents physical properties of plasticizers; Table II, areas under the time-sag curve at 76°F to 7 weeks; Table III, results of regression analysis on the areas; and Figure 1, a graphic portrayal of Table III and Equation (2). Table IV gives the areas under the time-sag curves at 135°F to 11 days.

The multiple regression calculated between the various areas in Table II at 76°F and the critical properties of surface tension and kinematic viscosity gave

$$A = 70.48 \frac{\sigma^{0.268}}{\nu^{0.116}} \quad (1)$$

as the best fit. A similar, rounded equation, also statistically valid, is

$$A = 87.15 \left(\frac{\sigma^2}{\nu} \right)^{\frac{1}{9}} - 6.09 \quad (2)$$

The plot of this equation is shown in Figure 1.

The addition of an exponential function of the solubility factor improved the fit. This equation is

$$A = 89.4 \left(\frac{\sigma^2}{\nu} \right)^{\frac{1}{9}} - 45.31 \exp \left[-3(\phi - 10.8)^2 \right] - 4.70 \quad (3)$$

where 10.8 is the solubility factor of an epoxy resin. The grouping

$\frac{2\sigma}{v}$ was also investigated by a regression analysis. The resulting equation

$$A = 111.89 \left(\frac{2\sigma}{v} \right)^{\frac{1}{8}} - 33.59 \exp \left[-2(\delta - 10.8)^2 \right] + 4.74 \quad (4)$$

had a worse fit than Equation (3), but was still statistically valid.

The presence of a negative exponential term is surprising. It indicates that a modicum of solubility of plasticizer in plastic is advantageous. Possibly a soluble plasticizer will swell the plastic and so heal the micro cracks through which a massive penetration of plasticizer to the glass-plastic interface could take place.

Results from Phase II are summarized in Table V. Details have been previously reported [7]. Parentheses indicate that the ring broke in a resin-poor area. Values given are actual results. The average of the two acceptable tests was used in the analysis of variance.

Table VI gives the results of the analysis of variance on data from Table V. The occurrence of a minimum in the plot of extension at break versus time has already been reported [7]. It has been further noticed that the time of the minimum correlates roughly with extension at break and also with the value of the solubility factor. Again it appears that a slight solubility of plasticizer in plastic may be beneficial in delaying massive penetration of the plasticizer to the glass-resin interface.

If the reciprocals of the sag-creep areas from Table II are plotted against these extensions, Figure 2 results for all plasticizers except tributyl phosphate (TBP) are almost a straight line.

A factor corresponding to Young's Modulus was also determined from stress-strain relationships of the rings. An analysis of variance indicated that time and plasticizer were significant variables. A significant quadratic factor was present in time, i.e., the increase in modulus at 9 months was significant in comparison with moduli at 3 and 21 months.

Rating of the plasticizers by moduli was generally the same as that by extension, except that triethyl phosphate (TEP) was less active and TEGDN more active.

Table VIII gives a comparison of values found in Phase I, Phase II, and Phase III for plasticizers common to all three phases. DBP alone is out of order.

Figure 3 shows plots of burst pressures versus the reciprocal of observed areas under the sag-time curve given in Table IV and also burst pressure versus extensions given in Table VII. Points for DPA, TEGDN, and the blank (air) are seen to be plotted in almost a straight line. The point for DBP does not. DBP does not seem normal, as can be seen by its plotted position in Figure 1 and its behavior elsewhere [8, 9].

A plot of moduli from Phase 2 versus reciprocals of areas, not shown, gives a similar result. DBP is again not normal.

b. Conclusions

An approximate prediction can be made between lowering of the burst pressure of a rocket motor case by a plasticizer and area under the sag-time curve of a coupon cut from that case and immersed in the same plasticizer. By extension of relationships, the decrease in burst pressures can be related inversely to viscosity and directly to the surface tension of the plasticizer.

The lowering of the burst pressure of a motor case by a plasticizer is considered minimal even after two years storage, amounting to less than 100 psi out of 2800 in the worst case. It is considered that in an actual condition, a motor case with a greater part of its strength due to glass fibers, a propellant with about 15 percent plasticizer and with a liner present, the rate of deterioration will be much slower, and will not reach a higher degree of deterioration. The same absolute value of deterioration in psi will be found in a case of much higher strength. No significant deterioration due to presence of plasticizer is to be expected during normal storage life, i.e., the life of the propellant.

Table I. Physical Properties of Selected Plasticizers

Plasticizer	\bar{M}	ρ_{25}^*	μ_{25}	σ_{25}^*	ν_{25}	δ
H ₂ O	18	0.997	0.89	71.9	0.893	23.5 [10]
DMP	194	1.189	17.2	45.6	14.48	10.8 [11]
DBP	278	1.042	11.3	36.2	17.5	9.4 [11]
TA	218	1.155	17.3	39.3	14.94*	10.3 [10]
TEP	182	1.068	1.6*	32.4	1.462*	9.0 [10]
DEP	222	1.115	6.8	40.5	10.8	9.8 [10]
TBC	360	1.046	23.9	33.3	31.0	9.0 [11]
DBT	262	1.087	65.6	33.6	62.3	9.5 [10]
TBP	266	0.971	3.7	30.0	3.50	9.0 [10]
EN	186	0.860	2.5	29.2	1.96	6.8 [11]
DBM	228	0.988	4.0	32.9	4.60	8.4 [11]
DBS	314	0.929	9.0	33.9	15.4	7.3 [10]
DPA	230	0.979	4.2	33.2	3.97	8.1 [10]
DBA	300	0.933	7.6	31.8	9.75	6.8 [10]
CO	933	0.951	620*	38.2	652*	7.0 [10]
TMETN	255	1.450	47.2*	48.9	32.5*	13.4 [10]
TEGDN	240	1.317	5.96*	47.2	4.52*	10.1 [10]
NG**	225	1.490	12.9	44.9	23.6	9.4 [10]

*Measured

**Desensitized with TA

Table II. Activity Ratings of Plasticizers at 76°F

Group	Plasticizer	Average Area	Confidence Level Between Groups (%)
1	H ₂ O	235.14	99.95
2	DPA	181.52	
	DBP	171.19	
	TEP	170.82	
3	EN	169.40	97.5
	TEGDN	162.58	
	DBM	158.66	
	TBP	153.29	
	TMETN	137.07	
	DEP	131.83	
	DBA	131.66	
	NG-TA	130.04	
	TA	129.61	
	DBS	128.43	
	Air	124.76	
	TBC	124.11	
4	DBT	117.36	95.0
	DMP	108.43	
	CO	97.48	

Table III. Correlation of Data in Table II

No.	Plasticizer	$\frac{\sigma^2}{v}$	A _{obs} *	A _{range} **	A _{calc} ***
1	H ₂ O	5800	235	±35	222
2	DMP	119	108	104-113	142
3	DBP	84	171	±25	136
4	TA	103	130	±22	140
5	TEP	718	171	±43	175
6	DEP	151	132	±23	144
7	TBC	36	124	109-139	124
8	DBT	18	117	113-121	114
9	TBP	257	153	±33	155
10	EN	435	169	166-173	165
11	DBM	235	159	137-180	154
12	DBS	75	128	120-137	135
13	DPA	278	181	±48	157
14	CO	2.2	97	88-107	89
15	TEGON	493	163	117-208	168
16	TMETH	73	137	129-145	134
17	NG-TA	65	130	126-135	133
18	DBA	104	132	128-136	140

*A_{obs} is the average observed area.

**A_{range} gives the one sigma variation, or the observed pair of areas.

***A_{calc} is calculated from Equation (2).

Table IV. Activity Ratings of Plasticizers at 135°F

Group	Plasticizer	Average Area	Confidence Level Between Groups (%)
1	TEP	315.50	90
2	DPA	283.85	
3	DBM	231.20	99
	DBS	216.70	
	EN	216.50	
4	TA	190.05	99
	DMP	188.00	
	DBT	183.00	
5	DEP	176.20	90
	TBP	167.25	
	Air	164.15	
	DBP	160.30	
	TBC	143.00	
	CO	123.80	

Table V. Effect of Plasticizers on Break Strength and Elongation at Break at 76°F

*Tensile strength is in pounds.
 **Elongation is given in thousandths of an inch.
 ***Estimated. Actual TS beyond the range of the instrument.

*Tensile strength is in pounds.

****Elongation is given in thousandths of an inch.**

***Estimated. Actual TS beyond the range of the instrument.

Table VI. Comparison of Plasticizers

Plasticizers	Extension (in.)	Confidence Level (%)	Minimum	δ	A_o	$\frac{1000}{A_o}$
Blank	10.92	90	At 21 months	-	124.76	8.02
TEGDN	10.64		At 21 months	10.1	162.58	6.15
DBP	10.27		At 12 months	9.4	171.19	5.84
EN	10.24		----	6.8	169.40	5.90
TEP	9.95		At 6 months	9.0	170.82	5.85
TBP	9.86		At 6 months	9.0	153.29	6.52
DPA	9.81		At 3 months	8.1	181.52	5.51

Table VII. Burst Strength of Cases in psi

Months	Blank			DPA			DBP			TEGDN		
0	2800	2900	3000									
6	3000	3400	2700	3000	3000	3200	3000	3200	3000	3200	3500	3200
12	2850	2860	2810	3000	2850	2810	3000	(2430)	2730	2770	2800	2910
18	2946	3000	2616	2634	2769	2688	2820	3054	3054	2820	2703	2793
24	2680	2900	2920	2730	2940	2450	3065	3035	2770	2765	2865	2775

Table VIII. Correlation of Burst Pressures

Plasticizer	Burst Pressure (psi)	Extension* (in.)	$\frac{1000}{\text{Sag Area}^{**}}$
DBP	2932	10.27	5.83
Blank (air)	2842	10.92	8.01
TEGDN	2800	10.64	6.15
DPA	2763	9.81	5.50

*Values of extension are from Table VII.

**Values of sag area are from Table II.

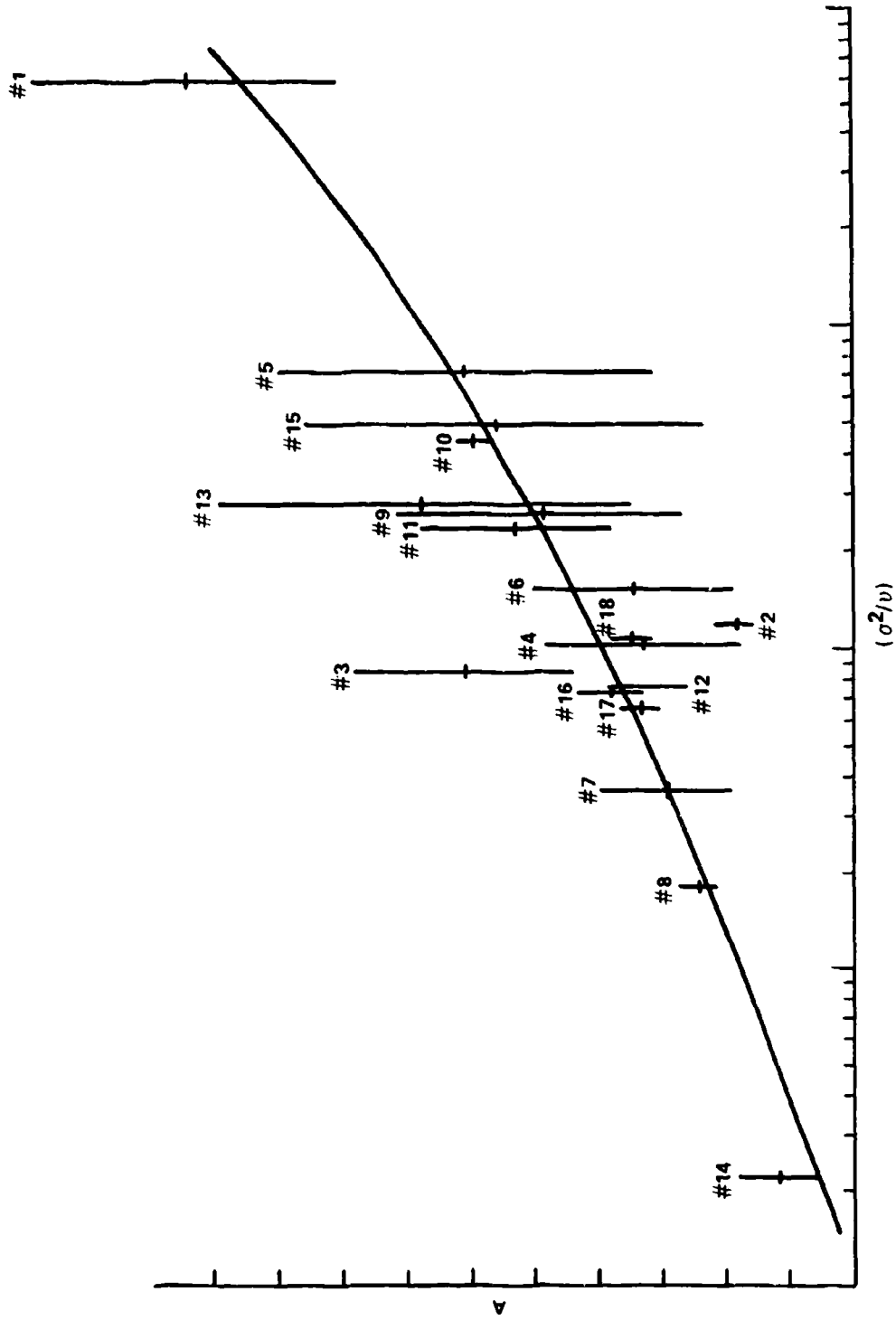


Figure 1.. Graphic Portrayal of Table III and Equation (2)

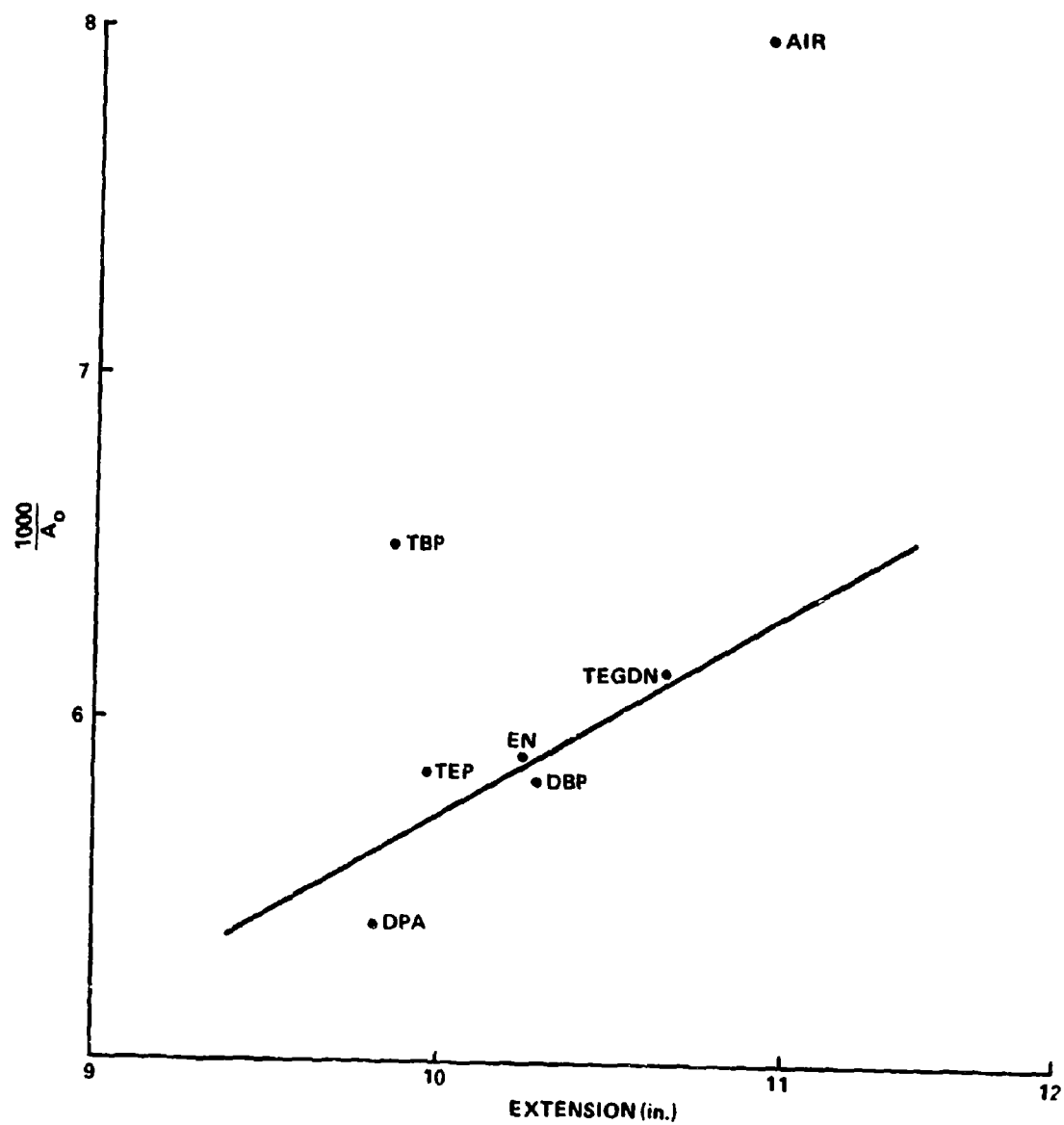


Figure 2. Sag-Creep Areas from Table II Plotted Against Extensions at Break

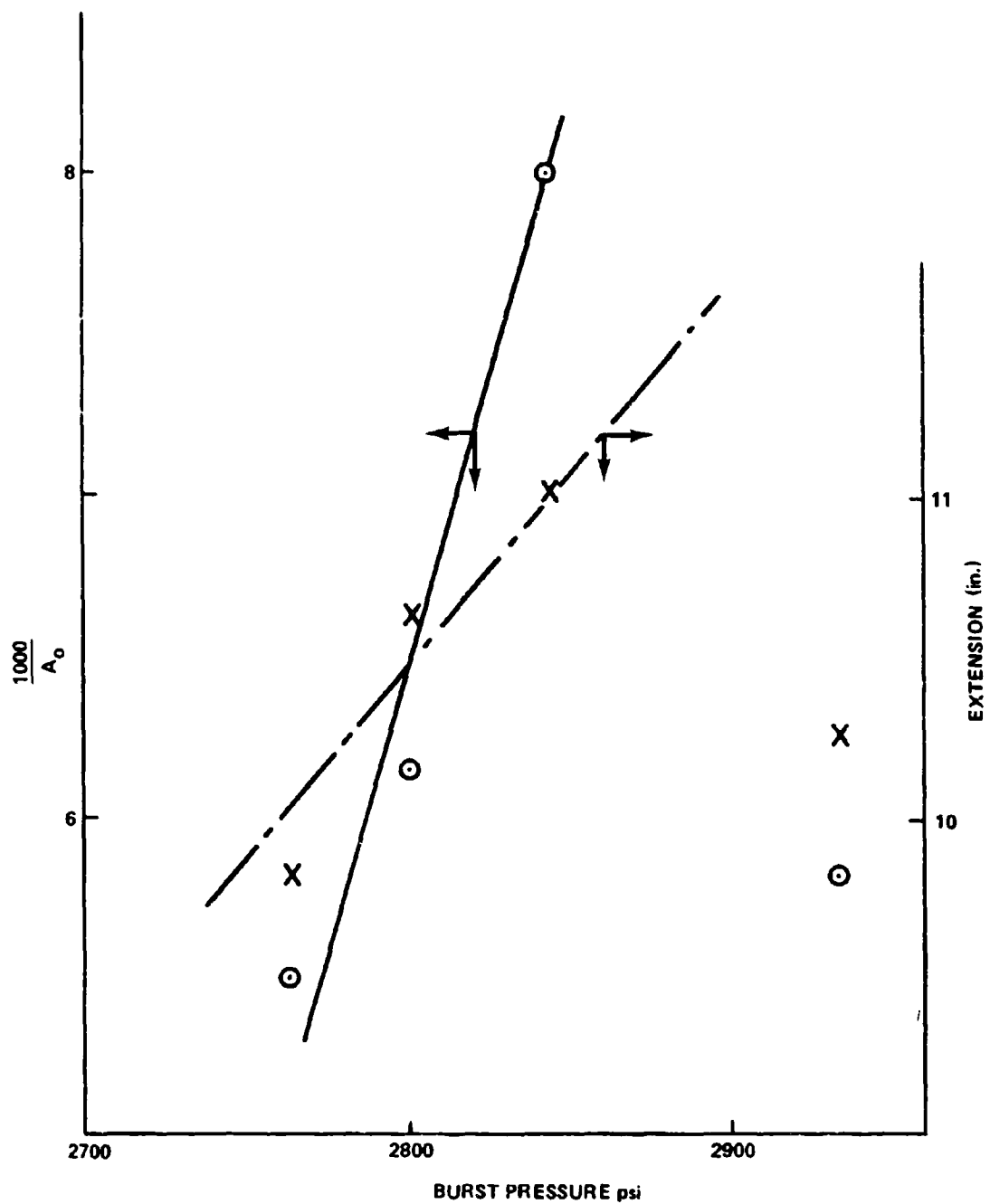


Figure 3. Burst Pressures Versus the Reciprocal of Observed Areas Under the Sag-Time Curves (Table II) and Burst Pressures Versus Extensions (Table III)

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